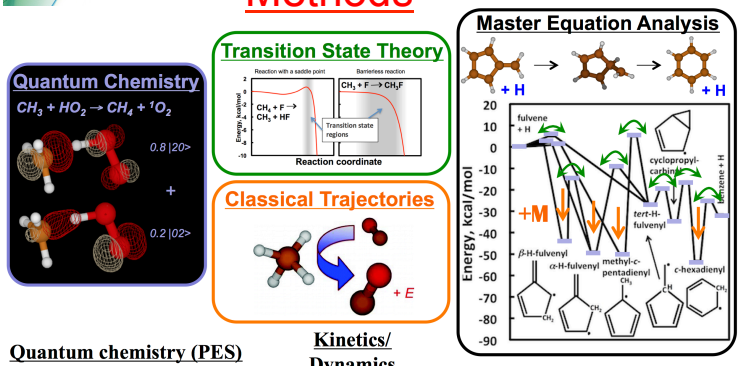
Predictive theories for combustion kinetics

Ahren Jasper, CRF, Sandia

Methods



Quantum chemistry (PES)
e.g., CCSD(T)/CBS//DFT
Geometries & Frequencies: Q ± ?
Reaction enthalpies: ΔH ± 1
Barrier heights: $V^{\neq}$ ± 1 kcal/mol

errors

Kinetics/ Dynamics
Microcanonical kinetics: $k(E,J)$ ± ?
Collisional Energy Transfer: $P(E,J;E',J')$ ± ?

errors

Competition
Phenomenological rate coefficients: $k(T,p)$ ± ?

A priori pressure dependence

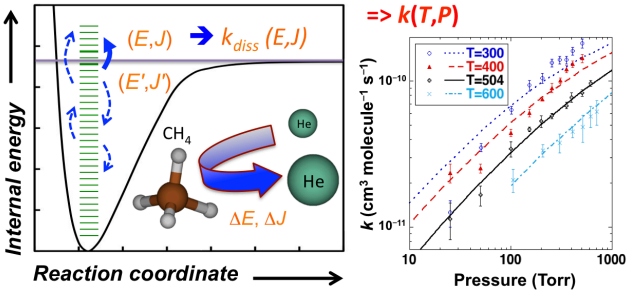


Figure caption. "Third-body" collisions activate unimolecular reactants, stabilize energized intermediates, and generally give rise to pressure dependence in chemical kinetics. Here, CH_4 + He collisions are shown schematically exchanging energy and angular momentum among the ladder of internal states (E,J) of methane. Collisions that activate methane above its dissociation threshold promote reaction. The mathematical treatment of these processes yields a priori predictions for the thermal rate coefficients that agree quantitatively with the experimental data.

Jasper, Pelzer, Miller, Kamarchik, Harding, Klippenstein, *Science* 346, 1212 (2014)

Spin-forbidden kinetics

MNST: A code for multidimensional nonadiabatic statistical calculations of spin-forbidden kinetics

Background

Existing methods for electronically nonadiabatic kinetics are significantly less well validated and less accurate than their electronically adiabatic counterparts. New methods are needed to enable predictive nonadiabatic kinetics calculations.

New theory

- Our previously developed multistate trajectories methods (available in the code DiNT) are used to characterize the physics of spin-forbidden reactions, with the goal of identifying physics that is neglected in existing statistical models.
- The "missing physics" includes multidimensional effects in the nonadiabatic transition probability, nonlocal electronic coherences, and nonstatistical effects.
- New statistical-based methods are being developed that include these missing physics. Most notably, we have developed a multidimensional nonadiabatic statistical theory that includes static and dynamical multidimensional effects.

Code

- Crossing seams are characterized via direct calls to electronic structure programs
- MNST calculations are based on multidimensional corrections calculated with DiNT
- Electronically nonadiabatic fluxes are produced for use as input to AITSTME

Jasper, Dawes, JCP 139, 154313 (2013)
Jasper, JPCA, in press (2015)

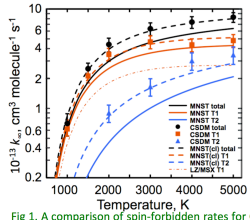


Fig 1. A comparison of spin-forbidden rates for O + CO → CO_2 calculated using: full-dimensional multistate trajectories (symbols), a simple one-dimensional statistical theory (green dotted line), and the new multidimensional statistical theory (blue solid line).

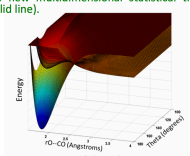


Fig 2. A representation of the 3 lowest-energy spin-orbit coupled potential energy surfaces of CO_2 calculated via MRCI+Q/CBS and fit with IMLS. IMLS is an automated surface fitting strategy interfaced with DiNT and was used to obtain the multidimensional correction as input for MNST.

Transport

Scientific Achievement

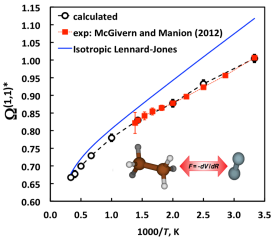
We demonstrated that very accurate transport properties can be calculated using classical trajectories and ab initio-based force fields.

Significance and Impact

Detailed chemical models of complex gas phase systems require thousands of kinetic and molecular parameters, most of which are either unknown or poorly known. Of these, transport properties are among the least well characterized. Our method provides a means of quantitatively predicting transport for thousands of previously uncharacterized species.

Research Details

- The collision integrals $\Omega^{(l,s)}$ are directly related to bulk transport properties (diffusion, viscosity, etc.).
- We calculate exact classical $\Omega^{(l,s)}$ using full-dimensional trajectories and ab initio-based force fields. The missing quantum effects are negligible, even for light species.
- The usual Lennard-Jones model for $\Omega^{(l,s)}$, in contrast, neglects inelasticity and anisotropy and has unrealistic repulsive forces. We quantified the errors due to these approximations.



The calculated collision integral for ethane + N_2 is in quantitative agreement with measured values of McGivern and Manion (NIST). This calculation has no adjustable parameters. The simple Lennard-Jones model is in fair agreement at high temperature, with larger errors are low temperatures.

U.S. DEPARTMENT OF ENERGY | Office of Science
A. W. Jasper, E. Kamarchik, J. A. Miller, and S. J. Klippenstein, *J. Chem. Phys.* **141**, 124313 (2014).
Sandia National Laboratories

Anharmonicity

mcPSI: A Monte Carlo phase space integral code for calculating accurate anharmonic vibrational properties of molecular systems

Background

Vibrational anharmonicity is often neglected in practical rate calculations of molecular systems. This ubiquitous (harmonic) approximation can result in significant errors, particularly at the high temperatures and energies relevant to combustion.

New theory

- Here we present an accurate and generally applicable approach for calculating vibrationally anharmonic molecular properties using classical Monte Carlo integration of phase space. The new method employs numerical evaluations of the Jacobian, allowing for the use of "chemist's coordinates" (stretches, bends, and torsions).
- Efficiency improvements are realized via decompositions of the full-dimensional vibrational state density into "intrinsic" pairwise, 3-mode, etc., state densities.

Code

- A stand-alone code that produces corrections to harmonic properties for use as inputs to the AITSTME code
- "Embarrassingly" parallel, e.g., direct (QCISD(T)/CBS) mcPSI calculations for vinyl took 14 h on ~1000 cores
- Availability: Coming soon

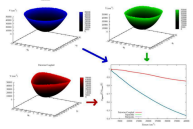


Fig 1. The potential energy surface associated with two modes of methane in the harmonic approximation (blue), the uncoupled anharmonic approximation (green), and without approxiamtion (red). We have demonstrated that the full-dimensional anharmonicity of methane can be recovered via evaluations of only the pairwise potentials.

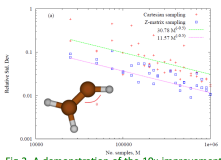


Fig 2. A demonstration of the 10x improvement in efficiency obtained using stretch/bend/torsion coordinates relative to the more commonly used Cartesian normal mode coordinates.

E. Kamarchik and A. W. Jasper, J. Chem. Phys. **138**, 194109 (2013).
E. Kamarchik and A. W. Jasper, J. Phys. Chem. Lett., submitted (2013).

Collaborators

Eugene Kamarchik (Sandia)
Richard Dawes (MST)
Stephen Klippenstein & Jim Miller (Argonne)

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